

Rheological Characteristics of UV Flexo Inks

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Abstract

The aim of this paper is to present some peculiar characteristics of UV flexo inks and to give a brief comparison with a classical water-based ink. Flow measurements were conducted on six free radical UV inks in order to clarify some of their rheological characteristics. These measurements were carried out on a cone-plate rheometer. Different models were applied to characterise the flow of these inks. Correlations between the parameters of the models were established. The influence of temperature and especially the determination of the activation energy of flow was examined. The thixotropic behaviour of inks was quantified and discussed. Finally, some measurements of surface tension are presented.

Introduction

Since the beginning of the 90's, UV flexographic inks have offered a new alternative to solvent and water-based inks. Although UV flexo inks are widely used in narrow web, such as label printing, wide-web applications remain minor. Apart from their solvent free composition, UV inks have many other advantages such as press stability, reduced waste, print quality, colour strength, improved rub and chemical resistances.

Unlike water-based inks, UV inks cure by photopolymerisation. They are 100% solid systems consisting of pigments, resins (oligomers), reactive diluents (monomers), additives.

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The many advances in composition of UV inks and the adaptation of the flexo process to this curing technology have made the development of these inks possible. Still, many works remain necessary to improve this process, namely, a thorough study of the ink transfer. A preliminary characterisation of the rheological properties of inks is required.

The aim of this paper is to present some characteristics of UV flexo inks and to give a brief comparison with a classical water-based ink.

Theoretical considerations

1. Modeling of shearthinning fluids flow

Printing inks are generally non-newtonian fluids with a shearthinning behaviour. The definition of this behaviour is the decrease of viscosity with an increase of shear rate. The Cross model (1965) gives a good description of this type of flow.

$$\left[\frac{\eta_0 - \eta}{\eta - \eta_\infty} \right] = (K \cdot \dot{\gamma})^n \quad (1)$$

where η_0 and η_∞ represent respectively the asymptotic values of viscosity at very low and very high shear rates. K is a constant parameter linked to a relaxation time and n , a dimensionless constant.

In many instances, it is convenient to make some approximations of equation (1). Thus, several practical models can be deduced from the Cross model, provided the range of application is correctly defined.

For example, if $\eta \ll \eta_0$ and $\eta \gg \eta_\infty$, the Cross model becomes:

$$\eta = K_1 \dot{\gamma}^{m-1} \quad (2)$$

which is the power law model, where K_1 represents the consistency (in Pa.sⁿ) and m , the power-law index. $m = 1$ means a newtonian behaviour and $m < 1$ a shearthinning behaviour.

Other approximations ($\eta \ll \eta_0$) lead to:

$$\sigma = \sigma_y + \eta_p \dot{\gamma} \quad (3)$$

well known as the Bingham model, where σ_y is the yield stress and η_p the plastic viscosity. Bingham model describes the flow of "plastic" fluids. These fluids will not flow until a critical stress (the yield stress) is exceeded. In practice, the yield stress is difficult to measure.

Some other equations are useful in modeling printing inks flow:

- Casson model (1959):

$$\sqrt{\sigma} = \sqrt{\sigma_0} + \sqrt{K\dot{\gamma}} \quad (5)$$

- Hershel-Bulkley model (1926)

$$\sigma = \sigma_0 + K \dot{\gamma}^n \quad (6)$$

where K is the consistency, σ_0 the yield stress and n the shearthinning index.

More recently, Pangalos and al. (1985) have developed another equation and applied it to news inks: the Bingham Exponential Decrease (B.E.D.) model. Its interest is to define four meaningful parameters, like the Cross model does, especially, the yield stress and the viscosity at high shear rates. The principle of this model is to share the flow curve in two parts:

- an exponential increase of the shear stress with the shear rate until a critical shear rate $\dot{\gamma}_C$,
- a Bingham behaviour beyond this critical shear rate

This leads to the equation (7):

$$\sigma = (\sigma_B + \eta_\infty \dot{\gamma}) - \sigma_L \exp - \lambda \dot{\gamma} \quad (7)$$

where η_∞ is the viscosity at high shear rates, σ_L is called the stress loss and is equal to $\sigma_B - \sigma_0$, and λ represents a characteristic time of the ink.

The critical shear rate is arbitrarily defined by Pangalos as equal to $5/\lambda$. σ_B is the apparent yield stress extrapolated from the Bingham equation. It is greater than the actual yield stress σ_0 , since the fluids under consideration are shearthinning. The practical significance of these constants is shown in Figure 1.

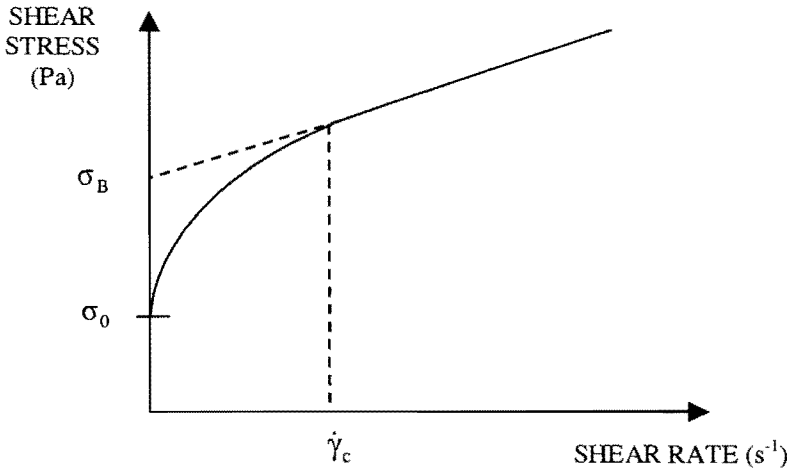


Fig. 1. Illustration of the significance of the B.E.D. model's parameters

2. Temperature-viscosity relationships

The characterisation of the temperature-dependence of viscosity is essential to get a better insight into the flow of printing inks. Two approaches have been developed on this topic. The first is based on the theory of absolute reaction rates (Eyring, 1935) and the second one on the free volume theory (Williams, Landel and Ferry, 1955). The first theory correctly fits with our systems, e.g. low DP-polymers. The second theory is not developed in this paper.

Theory of absolute reaction rates

This theory describes the flow process of a viscous liquid as the overcoming of a potential energy barrier by the molecular unit of this liquid.

It leads to the following equation linking viscosity and temperature:

$$\eta = A \exp(E_a / RT) \quad (8)$$

where A is a constant, R the gas constant, E_a the activation energy of flow, and T the temperature in K.

In the case of a shearthinning fluid, the energy activation of flow depends on the shear rate, as the viscosity is not constant. Thus, it is necessary to take into account the variations of E_a as a function of the shear rate (Vinogradov and Malkin, 1980).

3. Thixotropy

Time-dependent rheological properties, especially thixotropy, may also have a significant impact on the flow of printing inks. Thixotropy is the ability of an inelastic viscous liquid, submitted to a mechanical stress, to recover its initial equilibrium after this stress had been removed (Freundlich, 1928). This phenomenon is accompanied by an isothermal structural change. Many attempts to quantify thixotropy have been made. We chose the index of thixotropy defined by Chou and Bain (1988) to characterise our systems. It is based on a simple flow experiment: the shear rate is linearly increased from zero to a maximum value ("up curve") and then decreased from this value to zero ("down curve"). For thixotropic fluids, on a stress vs. shear rate plot, the two curves are different and present a hysteresis loop. The index of thixotropy is defined as the ratio of the surface of this hysteresis loop and the surface beneath the up curve.

Experimental procedure

1. Samples

Six commercial free radical UV flexo inks A, B, C, E, F, G, provided by SUN CHEMICAL, were examined in this work. Their exact compositions were not known. Only the pigment nature remained unchanged. For sake of comparison, a water-based ink was characterised.

2. Rheological characterisation

Rheological measurements were conducted on a rotative rheometer with the cone-plate geometry, in the steady-shear mode.

Measurements were carried out with a 4-centimeter, 1-degree cone for A, B, C inks and the water-based ink, and with a 2-centimeter, 4-degree cone for E, F, G inks. Increasing and decreasing shear rate scans (from 0 to 500 s⁻¹, during 1 min) were performed at temperatures varying from 10 to 60 °C, with steps of 5°C.

3. Surface tension measurements

Surface tension measurements were carried out on a Krüss tensiometer with the ring of Du Noüy. The surface tension is given by the equation:

$$\Gamma = \frac{P}{U} * F \quad (9)$$

where Γ is the surface tension in mN/m, P is the maximal force exerted on the ring, F a correcting factor taking into account the density of the fluid and U is equal to: $\pi(D_{in} + D_{ext})$, where D_{int} and D_{ext} are respectively the internal and external diameters of the ring.

Results and discussion

Flow behaviour

The six inks presented a similar shearthinning behaviour in the range of shear rates and temperatures examined. Figure 2 presents the up curves of the inks at 25°C.

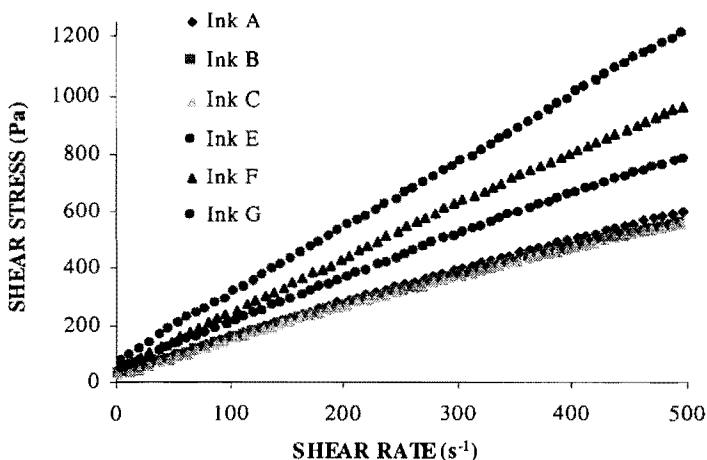


Fig. 2: Flow curves of UV flexo inks at 25°C

A, B and C have the same behaviour, with similar viscosities, whereas E, F and G have higher viscosities, which justify the use of a different geometry (cone with smaller diameter and higher top angle).

The Hershel-Bulkley model correctly describes the shearthinning behaviour of the 6 inks, with correlation coefficients around 0.99. For simplicity, an example of the results obtained for the parameters of the model at 20°C is given in Table 1.

Ink	σ_0 (Pa)	K (Pa.s ⁿ)	n
A	9.5	4.7	0.85
B	5.8	4.4	0.85
C	0.0	5.2	0.83
E	31.7	7.1	0.91
F	18.3	6.7	0.87
G	24.9	4.5	0.89
water-based	5.2	0.4	0.82

Table 1. Parameters of Hershel Bulkley model at 20°C

The yield stress values indicated in Table 1 are called "dynamic yield" values. According to Chou and Bain (1988), these values depend on the test conditions.

Generally, it turns out to be difficult to measure accurately the yield stress of a printing ink, especially with this type of rheometer which is not accurate enough in the range of very low shear rates.

Figure 3 shows differences in the evolution of the shearthinning index with temperature for inks B and F and the water-based ink. For A, B, C (represented by ink B on the figure, for simplicity) and the water-based ink, this index increases steadily and tends towards unity, which means that the behaviour of A, B and C tends to a Bingham behaviour when temperature rises. On the contrary, the shearthinning indices of E, F and G (represented by ink F) increase steadily and then decrease beyond a critical temperature located in the range of 25-35°C.

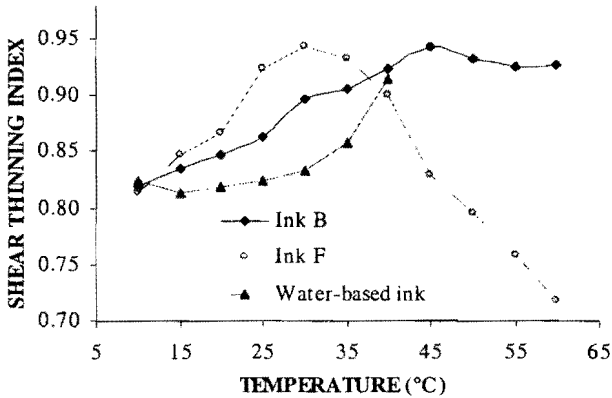


Fig. 3. Shearthinning index vs. temperature

Bingham Exponential Decrease model

An iterative method was used to determine the critical shear rate $\dot{\gamma}_c$ for which the Bingham model fits in the range $[\dot{\gamma}_c, 500s^{-1}]$. Thus, the parameters σ_B and η_∞ are determined. Then, the parameters λ and σ_0 are computed by a mathematical software.

The B.E.D. model fits also correctly with the experimental data of all the ink samples. The correlation coefficients of this 4-parameter model are greater than those obtained for the Cross model (less than 0.9 for Cross, in some cases).

The determination of the viscosity at high shear rate (η_{∞} in Pa.s) is more accurate with this model. Table 2 summarises the results at 20°C.

Ink	σ_B (Pa)	η_{∞} (Pa.s)	σ_0 (Pa)	λ (s)	$\dot{\gamma}_c$ (s ⁻¹)
A	77.1	1.7	22.2	0.012	44.2
B	70.8	1.5	12.9	0.019	65.2
C	79.7	1.7	0.0	0.022	60.8
E	131.2	3.8	55.9	0.012	65.6
F	105.8	2.8	30.4	0.021	15.4
G	74.7	2.2	17.4	0.040	0.0
water-based	11.9	0.1	5.5	0.020	0.0

Table 2. B.E.D. model's parameters at 20°C

The values of the yield stress are different from those calculated with Hershel-Bulkley model. But the absolute values are of the same order. The values of viscosity at high shear rates confirm the differences observed in the curves of shear stress vs. shear rates (Fig.2): E, F, G, respectively are more viscous than A, B, C whose viscosities are quite similar. The differences of viscosity at high shear rates between the water-based ink and UV flexo inks go from ten times to forty times higher.

The evolution of the other parameters of the B.E.D. model, $\dot{\gamma}_c$ and λ , are summarised on Figures 4 and 5.

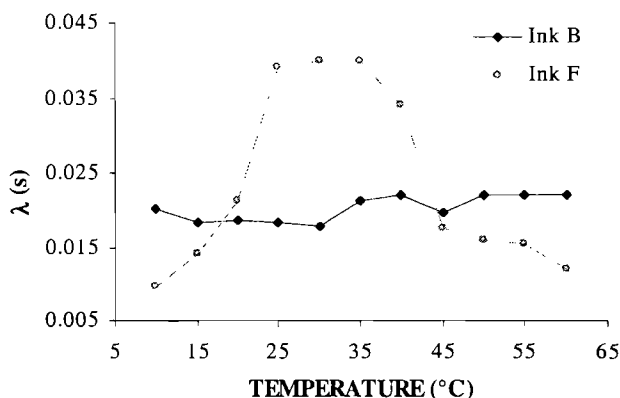


Fig.4. Characteristic time vs. temperature

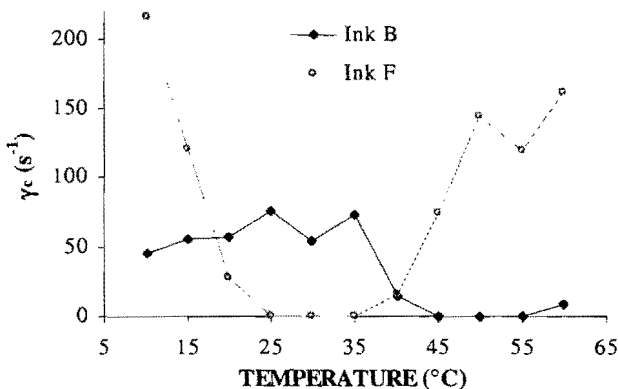


Fig.5. Critical shear rate vs. temperature

The characteristic times λ of inks A, B and C (represented on figures by ink B) are nearly constant, whereas those of inks E, F and G (represented by ink F) exhibit a maximum around 30°C. In the same time, the critical shear rates of E, F and G exhibit a minimum around 30 °C. $\dot{\gamma}_c$ is constant for A, B, C and tends to 0 beyond 40°C.

This result is coherent with the evolution described before: the flow behaviour tends to a Bingham behaviour with a temperature rise; if $\dot{\gamma}_c$ tends to zero, the global flow curve is modeled by a Bingham equation.

Viscosity

Table 3 summarises the measurements made at 500 s^{-1} and 20°C.

Ink	A	B	C	E	F	G	Water-Based
Viscosity (Pa.s)	1.8	1.7	1.8	4.0	2.9	2.3	0.2

Table 3. Viscosities of samples at 20°C and 500 s^{-1}

The measurements confirm the differences of viscosities evaluated by the B.E.D. model. Flexo UV inks examined had a viscosity varying approximately from 1.5 to 4 Pa.s. The viscosity of the water-based flexo ink was around ten times lower.

Activation energy of flow (E_a)

E_a values were obtained from viscosities measured at 500 s^{-1} . E_a was calculated from the slope of the curve $\text{Ln}\eta = f\left(\frac{1}{T}\right)$. The determination coefficients fit quite well, which confirms the validity range of absolute reaction rate theory. Some of the results are given in Table 4.

Ink	A	B	C	E	F	G	Water-Based
E_a (kJ/mol)	49.3	48.8	55.2	54.9	52.9	50.0	24.1

Table 4. Values of the activation energies of flow at 500 s^{-1} and 20°C

The values are quite similar. As a matter of fact, the values for UV flexo inks are two times higher than the value of the water-based ink. The viscosity of a UV flexo ink is more dependent from the temperature than a water-based ink, which can be explained by the chemical nature of the former.

Moreover, it is interesting to evaluate the influence of shear rate on the activation energy of flow. Thus, E_a was determined at seven different shear rates: 50, 100, 150, 250, 350, 450 and 500 s^{-1} . The results are shown on Figure 6. Only the curves of ink B and F are shown. Ink B is representative of inks A and C, ink F is representative of inks E and G.

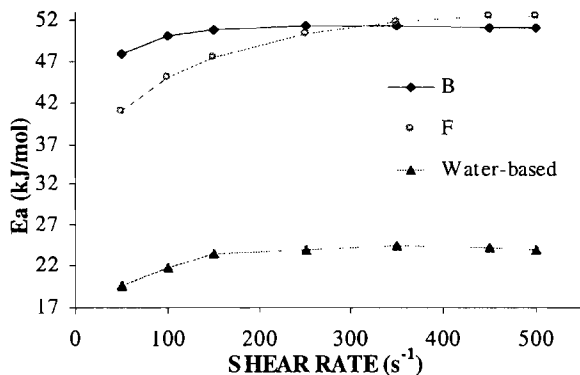


Fig. 6. Activation energy of flow vs. shear rate

The activation energy of flow of ink B and water-based ink increases and becomes constant beyond 200 s^{-1} . The variations of E_a for ink F are more significant. The determination of activation energy of flow for inks E, F and G is therefore influenced by shear rate. However, it can be assumed that the activation energy of flow becomes independent of the shear rate beyond 500 s^{-1} . Thus, it is more convenient to determine E_a from the values of viscosities at high shear rate, measured or deduced by the B.E.D. model (see Table 5).

Ink	A	B	C	E	F	G	Water-Based
E_a (kJ/mol)	49.7	49.1	55.4	58.3	56.5	54.2	24.7

Table 5. Activation energy of flow calculated from the viscosities at high shear rates

These results confirm the evolution of E_a with shear rate. For inks A, B, C, E_a is constant beyond 200 s^{-1} . For inks E, F, G, because of the shear rate ranges of the study, the shear rate where E_a becomes constant cannot be evaluated.

Thixotropy

The study of the thixotropy index shows again a fundamental difference of evolution between the two types of ink. While the thixotropy index of inks A, B, C (represented on Figure 7 by ink B) decreases with temperature, the index of E, F, G (represented by ink F) increases.

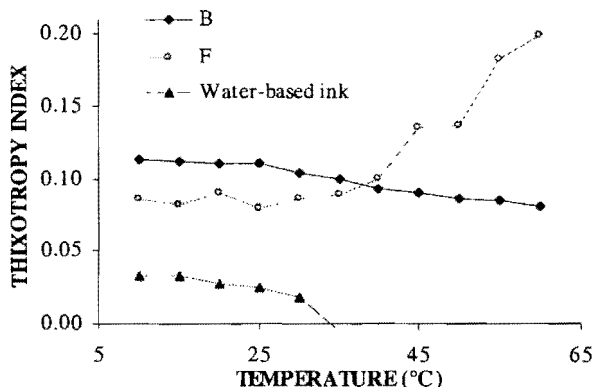


Fig.7. Thixotropy index vs. temperature

Figure 7 shows a clear-cut difference between UV flexo inks and water-based ink. The thixotropy index for A, B, C and water-based ink slightly decreases with a temperature rise: the occurrence of thixotropy is related to the formation of a structure between pigments in the ink, which tends to disappear when temperature rises, thanks to brownian motions. On the contrary, the increasing

of the thixotropy index of inks E, F and G was not expected. A better knowledge of the composition of inks is needed. However, these results emphasises again the existence of a critical temperature around 30°C for inks E, F and G.

Surface tension

Ink	A	B	C	E	F	G	Water-Based
Surface tension (mN/m)	23.3	37.8	35.3	39.1	38.5	38.3	33.8

Table 6. Surface tension of inks at 20°C

The results presented in Table 6 do not show high differences between inks B, C, E, F and G. These values are quite high compared to the surface energy of substrates currently used in flexo printing. It could affect the transfer of these inks. The surface tension value of ink A is surprising. Literature gives some values of UV ink surface tension in a range of 30-35mN/m. Up to now, no explanation was found to justify this value, because the exact composition of the ink A is not known. A specific surface modifier might have been added to the composition.

The surface tension of the water-based ink is a little higher than those given in literature. However, except for ink A, there is no aberration in these results. Other determination techniques should be developed to precise these results (for example, measurements of contact angle on a cured film of ink).

Conclusions

Some rheological characteristics of six commercial UV flexo inks were examined and compared to those of a water-based ink. The Bingham Exponential Decrease model gave a good description of the flow behaviour of these samples. It emphasised the role of temperature in flow of flexo UV inks. The dependence of their viscosity with temperature was examined, and the activation energy of flow was calculated. This energy depended on shear rate and became constant beyond a certain shear rate. The thixotropy of these samples has been discussed on the bases of a thixotropic index.

Comparison with a water-based ink was made. Meaningful differences in studied parameters such as shearthinning index, viscosity, activation energy of flow or thixotropy, were pointed out.

Experiments on the influence of temperature on the compositions of inks examined are still in progress. These results constitute a first step, in a wider study on ink transfer in the UV flexo process.

Acknowledgement

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